**The organic coating from a decorated human skull from the Neolithic site of Nahal Hemar (Israel): molecular evidence for the use of a vegetal substance**

# The organic coating from a decorated human skull from the Neolithic site of Nahal Hemar (Israel): molecular evidence for the use of a vegetal substance

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Human modeled skulls, a feature of the Pre-Pottery Neolithic B (PPNB) period in the Near East (ca. 8600 to 7000 BC), have been discovered in Nahal Hemar cave (Israel) and one of them exhibits a black organic coating applied in a net pattern. Recent molecular analyses of the organic coating using pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) and GC-MS have revealed the presence of cinnamate and benzoate derivatives suggesting the use of a styrax-type resin. A survey of the literature regarding the presence of cinnamate and benzoate derivatives led us to propose resins from Liquidambar orientalis or Styrax officinalis as possible botanical sources of the archaeological resin, both species growing in the Near East. GC-MS investigation of reference samples of fresh resins confirmed the presence of cinnamate and benzoate derivatives, indicating that such botanical sources were likely used among the ingredients of the organic coating of the skull. In addition, the triterpenoid distributions have been investigated in both the archaeological and botanical samples. The archaeological sample was shown to contain rather uncommon triterpenoids identified as 6- oxygenated derivatives of oleanolic acid based on their mass spectra. By contrast with the fresh resin of L. orientalis which does not contain such derivatives, the presence of the uncommon triterpenoids in the fresh resin S. officinalis indicated that the latter has been likely used during the preparation of the coating. Such a finding represents the earliest scientific evidence of a plant resin use in a cultural context.